



Remediation of soils contaminated with particulate depleted uranium by multi stage chemical extraction



Daniel E. Crean ^{a,b}, Francis R. Livens ^b, Mustafa Sajih ^b, Martin C. Stennett ^a, Daniel Grolimund ^c, Camelia N. Borca ^c, Neil C. Hyatt ^{a,*}

^a Immobilisation Science Laboratory, Department of Materials Science and Engineering, The University of Sheffield, UK

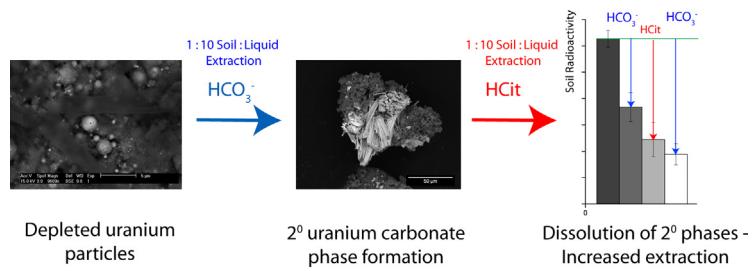
^b Centre for Radiochemistry Research, School of Chemistry, The University of Manchester, UK

^c Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland

HIGHLIGHTS

- Batch leaching was examined to remediate soils contaminated with munitions depleted uranium.
- Site specific maximum extraction was 42–50% total U in single batch with NH_4HCO_3 .
- Analysis of residues revealed partial leaching and secondary carbonate phases.
- Sequential batch leaching alternating between NH_4HCO_3 and citric acid was designed.
- Site specific extraction was increased to 68–87% total U in three batch steps.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 February 2013

Received in revised form 9 July 2013

Accepted 2 August 2013

Available online 12 August 2013

Keywords:

Depleted uranium

Chemical extraction

Remediation

Micro-focus X-ray diffraction

ABSTRACT

Contamination of soils with depleted uranium (DU) from munitions firing occurs in conflict zones and at test firing sites. This study reports the development of a chemical extraction methodology for remediation of soils contaminated with particulate DU. Uranium phases in soils from two sites at a UK firing range, MOD Eskmeals, were characterised by electron microscopy and sequential extraction. Uranium rich particles with characteristic spherical morphologies were observed in soils, consistent with other instances of DU munitions contamination. Batch extraction efficiencies for aqueous ammonium bicarbonate (42–50% total DU extracted), citric acid (30–42% total DU) and sulphuric acid (13–19% total DU) were evaluated. Characterisation of residues from bicarbonate-treated soils by synchrotron microfocus X-ray diffraction and X-ray absorption spectroscopy revealed partially leached U(IV)-oxide particles and some secondary uranyl-carbonate phases. Based on these data, a multi-stage extraction scheme was developed utilising leaching in ammonium bicarbonate followed by citric acid to dissolve secondary carbonate species. Site specific U extraction was improved to 68–87% total U by the application of this methodology, potentially providing a route to efficient DU decontamination using low cost, environmentally compatible reagents.

© 2013 The Authors. Published by Elsevier B.V. Open access under CC BY license.

* Corresponding author at: Immobilisation Science Laboratory, Department of Materials Science and Engineering, The University of Sheffield, UK. Tel.: +44 1142225470.
E-mail address: n.c.hyatt@sheffield.ac.uk (N.C. Hyatt).

1. Introduction

The development and deployment of armour piercing depleted uranium (DU) munitions has left a legacy of contaminated land in conflict areas and at test sites [1]. These areas may require long-term management and in some cases decontamination could be necessary to release the land for further use, or minimise risks to public health and environmental quality.

When a DU penetrator strikes an armoured target, 10–35% (maximum ~70%) of the mass is converted into aerosol [2] with median aerodynamic diameter of $d < 15 \mu\text{m}$ [3]. Uranium metal used in DU munitions is pyrophoric and oxidation of fragments and aerosols occurs on impact, typically producing UO_2 and U_3O_8 as the dominant species [4–7]. These oxidised particles settle in the surface environment close to DU impact sites, and have been observed in soils from Kosovo and Kuwait [8,9] as well as at test firing ranges [7]. DU is also introduced into the environment as intact penetrators which undergo corrosion [10], and in accidents such as fires [6]. This study focuses on the remediation of soils contaminated with DU impact particles, which due to their prevalence in the near surface represent the most likely route of near-term exposure for populations [11].

The effective remediation of land contaminated with DU particles is an on-going challenge. If contamination is heavy, e.g. at US army firing ranges [12] and some accident sites in Kuwait [6], bulk soil is disposed of as radioactive waste. This involves considerable expense, and methods to decontaminate bulk soils and separate DU contamination into a smaller volume are therefore attractive. Physical separation routes such as sieving have shown to be ineffective due to redistribution of U from weathering processes and agglomeration of DU aerosols [12]. Separation systems based on radioactivity are only useful for large fragments of penetrators due to the low specific activity of DU [13,14]. Chemical extraction could overcome these limitations for aerosol contamination by leaching DU phases from the soil. There are reports of effective chemical leaching of DU munitions contamination [15–17] – however, this has only been applied to a small number of sites and more comprehensive data on the effectiveness of chemical extraction to DU dusts across a range of environments is required. In this study chemical extraction is evaluated as a decontamination approach for two DU laden soils from a UK firing range at Eskmeals [7,18].

Decontamination by soil leaching has its basis in extraction of U from ores, where sulfuric acid or bicarbonate are common leaching agents [17,19]. Additionally, citric acid has been studied due to its strong aqueous complexation of uranyl (UO_2^{2+}) [20], low toxicity, low cost compared to other organic extractants [21], and potential for controlled degradation [22,23]. Under alkaline conditions, bicarbonate is modestly selective for uranium and causes less mobilisation of other metals (e.g. Fe, Zn, Mn) from soils than under acidic conditions [17,22]. Reported efficiencies for carbonate extraction range from 20 to 95% of total soil DU [15,24] depending on the site, demonstrating that local geochemical conditions influence the leaching performance. Site specific DU extraction by citric acid has a comparably wide range in efficiency (25–99% total soil U) [15,22], and sulphuric acid has also shown to be effective across a small number of sites [17].

In this study, the efficiency of chemical extraction for decontamination of DU munitions particulate at two sample sites from a UK firing range was evaluated. The aim was to use microscopic techniques for particle characterisation alongside bulk scale extraction experiments to provide a basis for improving the efficiency of extraction by process modifications. Particles from these sites were characterised prior to treatment by scanning electron microscopy (SEM) and sequential extraction to provide information on the initial geochemical disposition of U at these sites. Following

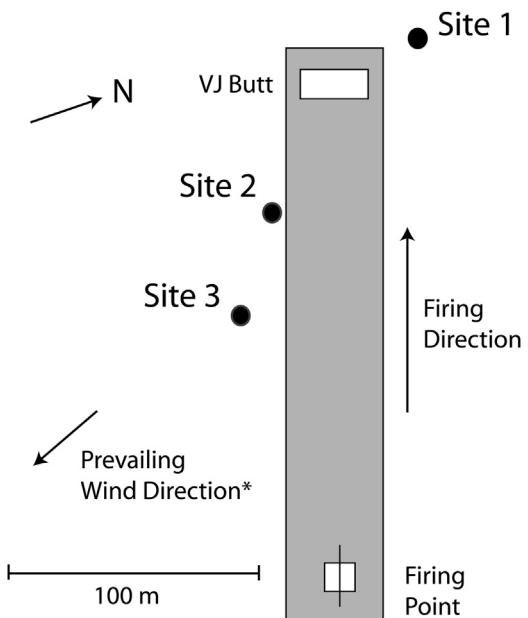


Fig. 1. Schematic of sampling locations within the VJ facility at MOD Eskmeals. The target and firing point are on a concrete apron. *Prevailing wind direction adapted from Oliver et al. [18].

batch extraction, remaining particles were non-destructively characterised by SEM and synchrotron X-ray micro-spectroscopy and micro-diffraction. These techniques were used to probe U behaviour in residues, and thus link residue particle properties with extraction efficiency. These data were then used to develop a more effective extraction methodology.

2. Experimental methodology

2.1. Site and soil sampling

Eskmeals in Cumbria, NW England, is a UK Ministry of Defence (MOD) firing range that was used in the development and testing of DU weapons from the 1960s to 1995. The area around the DU firing range (named the VJ facility) was exposed to fragments and aerosols from impacts, and approximately 3 ha is designated as a Controlled Radiation Area [18]. Soils from the site are useful for a remediation case study as contamination at the site has been well characterised, is relatively undisturbed due to restricted access and results from a constant, controlled firing direction [7,18,25].

Samples of soils from within the VJ radiation control area at MOD Eskmeals were collected in November 2011. Sampling was conducted in three areas (Fig. 1); Site 1 is a storage area for contaminated timbers used in the construction of targets, Site 2 is adjacent to a concrete apron area downwind from the target, and Site 3 comprises a spoil heap of disturbed sub-soil from post operational construction at the site. In all cases surface vegetation was removed and soil to a depth of 0.15 m from an area of approximately 0.05 m² (total soil volume ~3 L) was sampled into plastic bags, which were sealed for transfer to the laboratory. All samples were air dried at 40 °C and sieved to remove particles above 2 mm. The remaining soil was homogenised by hand, divided into representative portions using the cone and quarter method, and dry stored in sealed containers under ambient conditions. DU particles were localised for spectroscopy and microscopy using a sample splitting technique and autoradiography [7]. Soil pH was measured in 1:5 soil:water extracts shaken for 2 h [18] using a WTW pH 315i (Exptechn).

Table 1

Sequential extraction reagents and conditions. For more detail, see the BCR extraction scheme as described by Ure et al. [26].

Step	Extraction procedure
1 – Exchangeable	40 ml 0.1 mol/l acetic acid, 5 h
2 – Fe/Mn Bound	40 ml 0.1 mol/l $\text{NH}_2\text{OH}\text{HCl}$ acidified to $\text{pH}=2$ with conc. HNO_3 , 16 h
3 – Oxidisable	10 ml 30% (w/v) H_2O_2 , 1 h at room temperature and 1 h at 85 °C. Solution taken to dryness and repeated. Residue reacted overnight with 50 ml ammonium acetate, acidified to $\text{pH}=5$ with conc. acetic acid
4 – Residual	10 ml 8 M HNO_3 at 80 °C for 4 h. Residue taken to dryness and repeated

2.2. Sequential extraction

The sequential extraction procedure follows the BCR scheme [26] as it has been previously applied to uranium speciation in soils [25–27]. The BCR scheme has three steps in which the speciation of the element of interest is defined as exchangeable, reducible and oxidisable [26]. The residual material is then analysed by total digestion or aggressive acid leaching to determine the mass balance. Here the residual phase was evaluated by repeated digestion in hot nitric acid. Triplicate 1 g samples of dried soil from site 1 and site 2 were studied for U partitioning (Table 1). After each extraction step, the sample was centrifuged for 40 min at $4000 \times g$, the supernatant taken to dryness and then made up to 5 ml in 2% HNO_3 . Total DU soil concentration was evaluated by subjecting triplicate 1 g samples of fresh soil to step 4 only, as described previously [7,28]. All extraction phase U concentrations were determined by ICP-AES.

2.3. Batch leaching

Dried soil was subsampled using the cone and quarter method and a mass of 1 g taken for each leaching experiment. Initial soil activity was determined by autoradiography. Triplicate 10 ml leaching experiments were prepared with solutions of 0.5 M NH_4HCO_3 , 0.1 M citric acid and 0.1 M H_2SO_4 , conducted in sealed 50 ml vials with an air headspace. Samples were left to react for one week at ambient temperature with agitation on a shaker table. After reaction, the supernatant was separated from bulk soil by filtration, followed by acidification to $\text{pH} 2$ with concentrated nitric acid and analysis by ICP-AES. Residual soils were dried and remaining soil activity was determined by autoradiography. For site 1 samples, the residue from batch extraction was subject to step 4 (Residual) as described above.

2.4. Solid and liquid uranium concentration analyses

Bulk soil activity was determined non-destructively by autoradiography. 1 g soil samples were spread onto 8 cm diameter filter papers and exposed to a phosphor storage screen for 21 h, and the screen read using a phosphor imager (Typhoon Imager, GE Healthcare). The pixel intensity across each sample was summed, along with an equivalent background region of the plate, allowing estimation of total radioactivity. This process was repeated before and after remediation experiments. The decontamination factor, as used here, is defined as the amount of radioactivity (determined by autoradiography) removed from soil divided by the initial activity, and is equal to 1 for complete decontamination, and zero for no decontamination. The decontamination factor was also calculated using extracted U mass in the leachate and residual U mass by acid digestion (Step 4, Table 1) for site 1 samples. Good agreement between yields measured by these two techniques was observed.

Leachate uranium concentrations were analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Perkin-Elmer Optima 5300 dual view ICP-AES. Standards were analysed at 0.1, 0.5, 1 and 10 ppm U, prepared by dilution of a 1000 ppm standard solution (Sigma Aldrich, UK). Matrix matched samples for each remediation experiment were analysed at 1, 5 and 10 ppm. Analysed U standards were within 3% of the expected value.

2.5. Environmental scanning electron microscopy (ESEM)

Scanning electron microscopy was used to investigate particle morphology and composition. Samples were mounted on adhesive carbon pads and were not coated prior to analysis. The ESEM (FEI XL30) was used in high vacuum with accelerating voltage of 15 kV and back-scattered electron (BSE) imaging to identify areas of high atomic number elements. The composition of high-Z particles identified by BSE imaging was investigated using Energy Dispersive X-Ray (EDX) analysis.

2.6. μ -XRF, μ -XRD and μ -XANES

Synchrotron radiation microfocus X-ray analyses were conducted at the MicroXAS (X05LA) beamline at the Swiss Light Source (SLS). The photon energy range is 4–23 keV, and the beam line can deliver monochromatic X-rays by means of a Si (1 1 1) double crystal monochromator. In these experiments, the spot size was approximately 5 μm (h) \times 2 μm (v). Samples were mounted on a motorised x-y-z stage which allows scanning in the beam for mapping. The stage was positioned at a 25° angle to the incident beam. Samples were mounted on carbon pads or Kapton tape.

X-ray fluorescence (XRF) was measured using a Si(Li) detector (KETEK) mounted at 90° to the incident beam. XRF spectra were monitored to localise particles containing U in the beam for analysis. X-ray diffraction (XRD) was measured using a PILATUS 100K hybrid pixel array detector [29] mounted 46 mm behind the sample, with a tungsten beamstop in place. The detector tilt and distance to the sample were calibrated by measurement of a silicon standard. Phases were identified with reference to ICSD PDF-2 database records, and the record numbers are given in the corresponding figures. The experimental setup was chosen such that XRF and XRD measurements could be made concurrently, with a monochromatic beam of energy 17.300 keV ($\lambda = 0.7167 \text{ \AA}$). Uranium L_{III} edge ($E_0 = 17.166 \text{ keV}$) XANES (X-ray absorption near edge structure) spectra were recorded in fluorescence mode by recording the U $\text{L}\alpha$ emission (13.614 keV) and tuning the monochromator energy from 16.900 to 17.500 keV. Energy calibration was performed with respect to the K-edge of a yttrium foil (17.038 keV) and fluorescence XANES spectra of standards of UO_2 , U_3O_8 and UO_3 were also recorded.

3. Results and discussion

3.1. Soil characterisation

3.1.1. Bulk soil properties

A soil sample from a nearby soil horizon was characterised for local bulk soil characteristics including mass particle size distribution, cation exchange capacity, and total organic carbon using standard techniques (Table 2) [30]. Soils from the area are characterised as raw dune sands [7,18]. Site 1 soil pH was 5.5, Site 2 was 7.6 and Site 3 was 6.5. These agree well with previously published soil pH data in the range 5.6–7.8 [18] for the Eskmeals site.

3.1.2. Total uranium

Soils from sample site 1 have the highest level of contamination ($320 \pm 40 \text{ mg U/kg}$), with approximately an order of magnitude

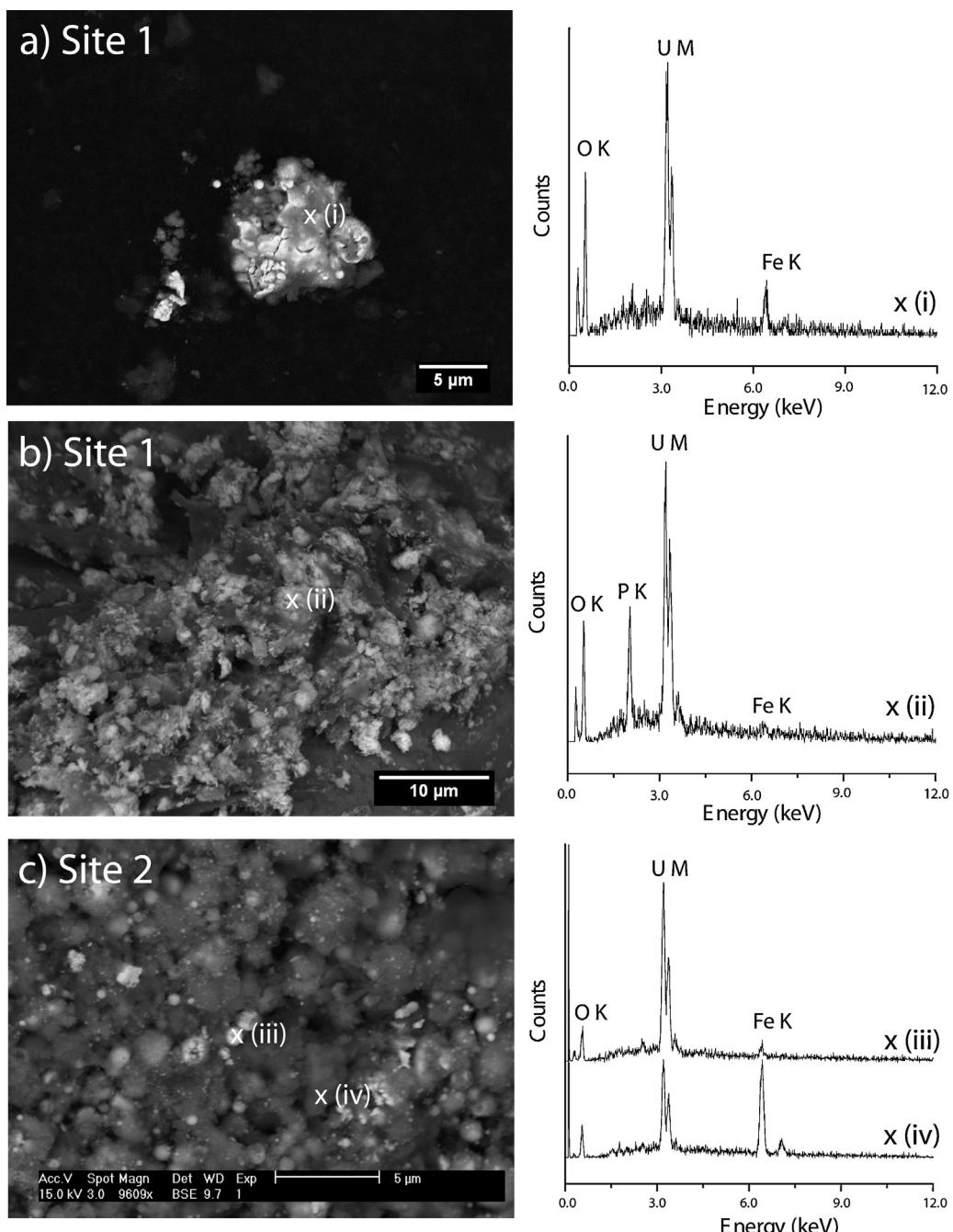


Fig. 2. Backscattered micrographs and EDX spectra of DU particles present in Eskmeals soil from sample site 1 (a) and (b) and sample site 2 (c). DU rich particles appear brightly in BSE imaging, and the presence of U in these areas was verified by spot EDX analysis. The X in micrographs shows the position of the electron probe during EDX data collection.

Table 2

Bulk soil particle size distribution and organic carbon for Eskmeals area soil. The soil total bulk organic carbon was 0.2%, and cation exchange capacity (CEC) was determined as 0.6 Meq/100g.

Size fraction (µm)	% Mass abundance	% Organic carbon
250–2000	2.1	1.5
125–250	87.7	0.03
63–125	7.8	0.2
32–63	0.7	1.1
2–32	1.4	6.4
<2	0.2	10.6

greater uranium burden than sample site 2 (37 ± 4 mg U/kg). Background concentrations of U around the site are reported between 0.2 and 1.7 mg U/kg [25], close to that measured at site 3 (2.2 ± 0.5 mg U/kg). The higher concentration in site 1 soils is probably linked to the storage of heavily contaminated timbers from the target hutch, whereas site 2, located downwind from the target, is more typical of DU contamination arising from settling and scattering of impact particles [9].

Site 2 is in a similar location to “Pad Edge” samples studied previously [18], and the U concentration is of similar magnitude to the reported concentrations in the range 60.8–72 mg U/kg [18,25,31]. Higher concentrations and large variation reported in some sample sites close to the firing Pad Edge (“Pad Edge A” – 282 ± 142 mg/kg

[18]) were not observed in this study, which suggests that the pattern of contamination at the site is highly spatially heterogeneous, with localised “hot-spots” of elevated DU concentration.

3.1.3. Scanning electron microscopy

Electron microscopy was used to study the morphology, microstructure and elemental composition of DU aerosol particles in the soil samples. Features which appeared bright in back-scattered electron (BSE) imaging were examined for elemental composition by EDX analysis.

Aerosol particles produced by U impact often have a characteristic spherical primary morphology linked to melting of metallic U during high temperature impact events [4]. Particles with this characteristic morphology were observed in soils from both sample sites (Fig. 2). The size range, morphology and elemental composition of particles observed in this study are broadly similar to those observed in live firing tests [4,32] and from conflict zones [5,6,33]. In addition, U-rich areas with platy crystal habit were observed in soils from site 1 (Fig. 2b) suggesting formation of secondary phases as a result of particle weathering.

In some cases, large numbers of DU particles were observed adhered to larger ($<200\text{ }\mu\text{m}$) silicon-rich particles, probably sand grains, the surface of which is shown in Fig. 2c. This is a complicating factor for remediation by physical separations such as sieving—although DU particles have a characteristic size range ($<15\text{ }\mu\text{m}$, [3]), adhesion processes make it impossible to effectively separate these particles in soil fines fractions, which may explain the poor reported performance of particle size based physical separation processes for DU decontamination [12].

3.1.4. Sequential extraction

The fraction of U extracted in each step of the sequential BCR scheme is similar in both soils (Fig. 3), despite an order of magnitude difference in the total U concentration. This indicates that at both sites the bulk geochemical behaviour of the DU contamination is similar; with most of the inventory partitioning into BCR defined oxidisable and residual phases. These phases require aggressive extraction conditions for solubilisation, indicating that the majority of the U inventory is chemically resistant to dissolution.

Although the BCR oxidisable soil fraction is normally interpreted as species bound to sulphides or organic matter [26], this interpretation is not valid for samples containing U(IV)-oxide phases, which are readily solubilised by H_2O_2 [19]. As primary particle morphologies are observed in both site soil samples (Fig. 2), it would be expected that a substantial fraction of primary U(IV) phases persists in these soils, consistent with the abundance of oxidisable uranium at both sample sites.

Table 3

Remediation extraction data for DU in sample site 1 and sample site 2 soils exposed to 0.1 M Citric Acid, 0.1 M H_2SO_4 and 0.5 M NH_4HCO_3 . The decontamination factor is defined as the amount of net radioactivity (for autoradiography data) or uranium mass (for ICP-AES data) removed as a fraction of the total net radioactivity or uranium mass. Error estimates are ± 1 standard deviation of triplicate analyses.

	Extraction reagent		
	0.1 M Citric acid	0.1 M H_2SO_4	0.5 M NH_4HCO_3
Sample site 1			
Decontamination factor (autoradiography) ^a	0.3 ± 0.1	0.2 ± 0.05	0.4 ± 0.1
U extracted ^b (μg)	135 ± 28	80 ± 31	173 ± 35
U remaining ^c (μg)	172 ± 27	286 ± 37	165 ± 29
Decontamination factor ^c	0.4 ± 0.1	0.2 ± 0.1	0.5 ± 0.1
Sample site 2			
Decontamination factor (autoradiography) ^a	0.4 ± 0.1	0.1 ± 0.1	0.5 ± 0.2
U extracted ^b (μg)	23 ± 3.9	7.5 ± 2.8	29 ± 12

^a Determined by autoradiography.

^b Determined by ICP-AES measurement of the leachate.

^c Determined by nitric acid digestion of the residual soil.

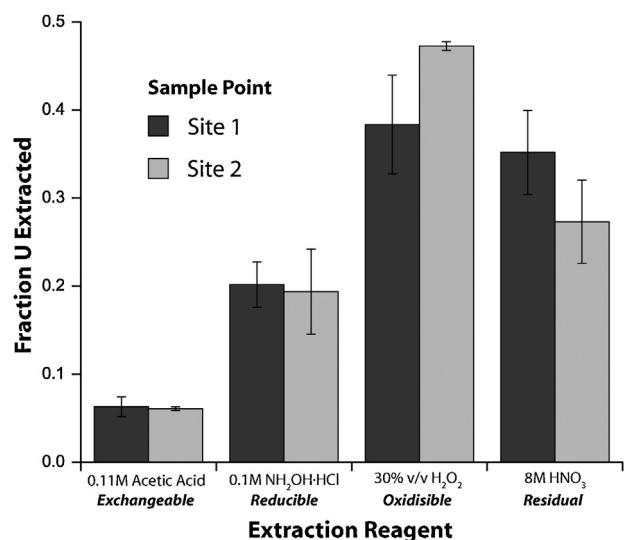


Fig. 3. U fractionation between operationally defined speciation classifications for two soils at the Eskmeals site. Total U is $320 \pm 40\text{ mg/kg}$ for Site 1, and $37 \pm 4\text{ mg/kg}$ for Site 2. Error bars are one standard deviation of triplicate analyses.

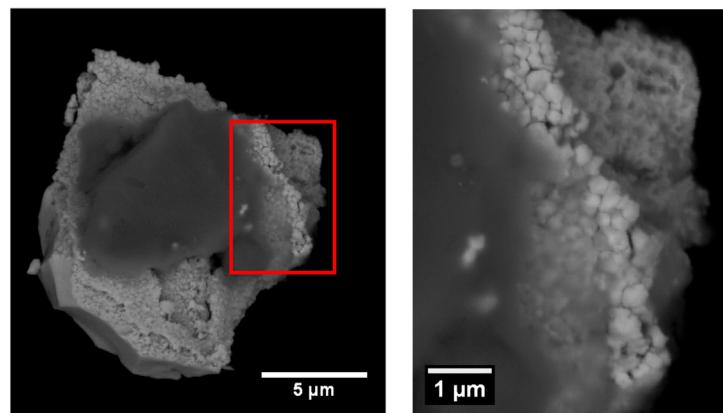
The presence of U extracted in exchangeable and reducible fractions suggests that some U(VI) alteration products are present, as U(IV) oxides exhibit low solubility in non-oxidising acids such as acetic acid and with reducing agents such as $\text{NH}_2\text{OH}\cdot\text{HCl}$. U(VI) oxy-hydroxide species are a typical corrosion product of DU(IV) phases in oxic surface moist environments [34] and are readily solubilised by acetic acid [35], and may account for the minor (6%) exchangeable fraction of the U inventory. The reducible soil fraction accounts for U bound to poorly crystalline Fe/Mn phases, and comprises approximately 20% of the total U at both sites. Processes such as sorption and co-precipitation of U(VI) with Fe(III) hydrous oxides, which can occur in U contaminated environments, would produce a ‘reducible’ extraction inventory of U in these soils [36]. Although there are uncertainties in the selectivity of BCR extraction reagents, the results for the exchangeable and reducible fractions give a first order estimate of the extent of labile U(VI) species as approximately 25%.

3.2. Remediation of contaminated soils by chemical extraction

3.2.1. Batch extraction

Batch remediation data for sample site 1 and sample site 2 are shown in Table 3. The mass of U extracted from 1 g soil samples is measured from the leachate U concentration, determined by

Site 1 - Treated Particle 1



Site 1 - Treated Particle 2

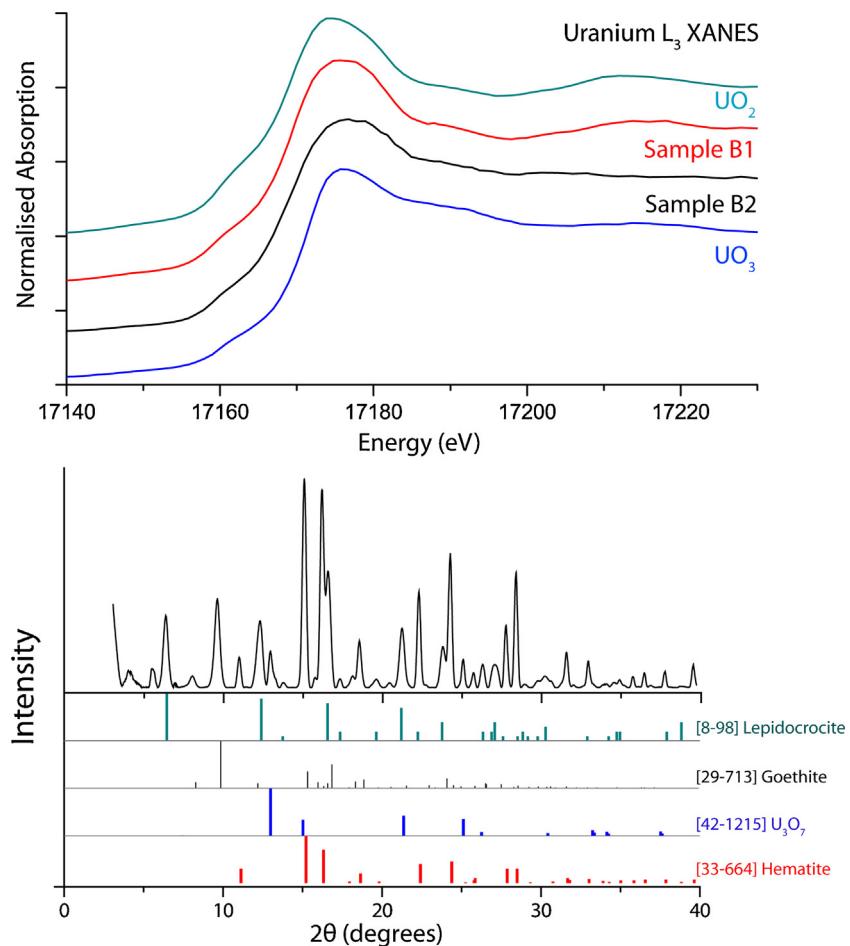


Fig. 4. Backscattered electron micrographs (treated particle 1), XANES spectra and XRD pattern with corresponding ICSD PDF-2 database numbers (treated particle 2) of residual primary particles. The micrographs show morphology suggestive of a partially leached oxide particle, including grain boundary etching. This is supported by XRD and XANES analyses showing the presence of U_3O_7 and U(IV) in some soil residues.

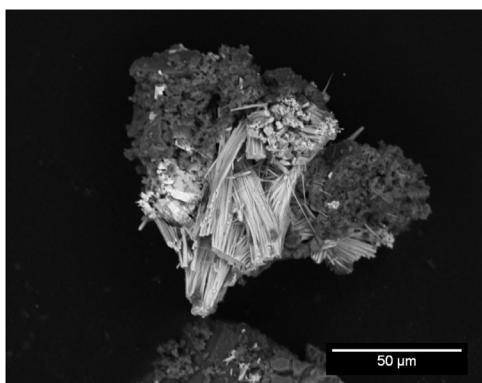
ICP-AES. The trend in U mass (μg) extracted agrees well with the autoradiography decontamination factor.

The data indicate that ammonium bicarbonate is the most effective extractant. Extraction in citric acid is somewhat less effective (~20%), and dilute sulfuric acid has the lowest extraction efficiency. Extraction efficiencies are similar across both sample sites, which is consistent with similarities in sequential extraction data (Fig. 3). Reasonable agreement was also observed between

decontamination factor determined by autoradiography and dissolution of residual soils (Table 3), with the same trend in extraction efficiencies observed in both data.

These data show that chemical extraction can remove substantial portions of munitions DU from soils, but that additional optimisation would be required to achieve complete decontamination. The amount of DU removed is comparable to similar extractions performed on contaminated soils from a US military

Site 1 - Treated Particle 3



Site 1 - Treated Particle 4

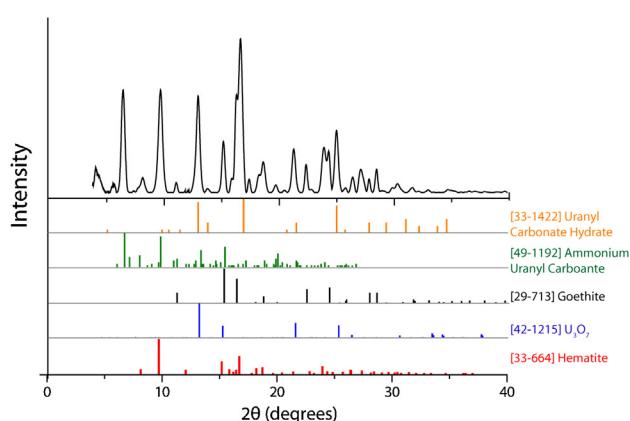


Fig. 5. Electron micrograph of particle showing acicular crystal habit (treated particle 3) consistent with uranyl-carbonate species, and powder XRD pattern with corresponding ICSD PDF-2 database numbers from a different particle (treated particle 4), showing the presence of two uranyl carbonate phases.

site, in which decontamination factors for citric acid range from 0.35 to 0.6 and from 0.3 to 0.6 for bicarbonate, with ambient dissolved oxygen as the oxidising agent [15]. The good agreement with previously reported extraction efficiency suggests that this approach may be applicable to other instances of depleted uranium contamination.

3.2.2. Residual particle analysis

The decontamination factor is determined non-destructively by autoradiography, allowing the treated soil to be recovered for analysis. In order to optimise and improve the process, information on the U phases which remain after extraction is required.

A repeat set of dried bicarbonate treated soil samples from site 1 were examined by autoradiography, which revealed that particulate residues were still present. Particles from this test were selected as bicarbonate offers the most effective U extraction, and site 1 had the highest U concentration and lower decontamination factors than site 2. The separated particles were analysed by electron microscopy, microfocus-XRD and microfocus-XANES at the U-L_{III} edge.

Electron micrographs reveal two distinct particle morphologies, one group consistent with primary aerosol particles (Fig. 4), and a second group which has a structure suggestive of secondary phase formation (Fig. 5). Indications of dissolution are observed in primary particles, in particular preferential grain boundary dissolution evident in the etched grain structure in Fig. 4. This phenomenon is also observed in the oxidative dissolution of unburnt civil nuclear fuel grade UO₂ [37]. The modification of the particle microstructure indicates that some dissolution occurs, but not to completion on the timescale of these batch experiments. XRD data are also consistent with the presence of unreacted primary species, as U is present as U₃O₇ which agrees well with comparable data from untreated particles at the Eskmeals site [7]. Micro-XANES data show that the predominant oxidation state in the samples is U(IV), as spectra edge shifts, white line positions and post edge oscillations are similar in character to the UO₂ standard (Fig. 4). This is consistent with XRD data showing U₃O₇, and previous studies of DU particulate which show U to be present as U(IV) in untreated particles [5,6].

The conservation of primary oxide species and evidence of partially leached microstructure suggests that although these phases are amenable to carbonate extraction, they are dissolved slowly, requiring longer than the experimental timescale for complete dissolution.

The second morphology is not observed in untreated material. U-rich particles with an acicular habit (Fig. 5) are consistent

with the formation of uranyl-carbonate secondary phases [38]. XRD analysis confirms the presence of uranyl carbonate hydrate phases and ammonium uranyl carbonate, the latter presumably due to the high concentration of ammonium in the 0.5 M NH₄HCO₃ primary leaching solution.

The formation of secondary phases may explain the slightly reduced extraction efficiency in site 1 soils (Table 3), and it is probable that this process will be an important control on extraction efficiency in highly contaminated soils.

3.3. Alternating batch extraction

The presence of secondary uranyl carbonate hydrate phases suggests that a single batch extraction is not the best approach to removing as much DU as possible from Eskmeals soils, and an alternating basic/acid washing procedure could improve extraction by rapidly dissolving secondary phases.

The results of a three-step bicarbonate/citric acid/bicarbonate leaching process are presented in Fig. 6. The first step extraction in NH₄HCO₃ removes around 50% of the uranium inventory at both sites, as expected from the single step bicarbonate leaching tests. For the second extraction in 0.1 M citric acid, additional uranium is removed from site 1 samples, but negligible uranium is released from site 2 soils. This may reflect a larger mass of secondary uranyl carbonate hydrate phases in site 1 samples, which are then dissolved under acidic conditions.

An additional bicarbonate step was trialled to test the susceptibility of residual particles to further leaching. In both sites, a second bicarbonate extraction resulted in the removal of additional uranium from the soils. This suggests that different fractions of the DU inventory are accessible to different leaching reagents, and that bicarbonate extraction is more effective at removing residual phases from both site soils. The total uranium removed as a percentage of the initial activity in the three step leaching process was 68 ± 14% for site 1 and 87 ± 7% for site 2, which represents a substantial improvement on single step leaching.

Representative autoradiographs of soil samples from each site are presented in Fig. 6. This technique allows the dissolution of particles to be tracked across each extraction stage. The autoradiographs of site 1 soils show that large agglomerate particles are readily broken down and slowly leached during multi-stage extraction, whereas smaller particles in site 2 soil are dissolved more rapidly. The decreasing activity of the fragments in sample 1 between washes suggests that these particles would eventually be completely dissolved. These results demonstrate that enhanced

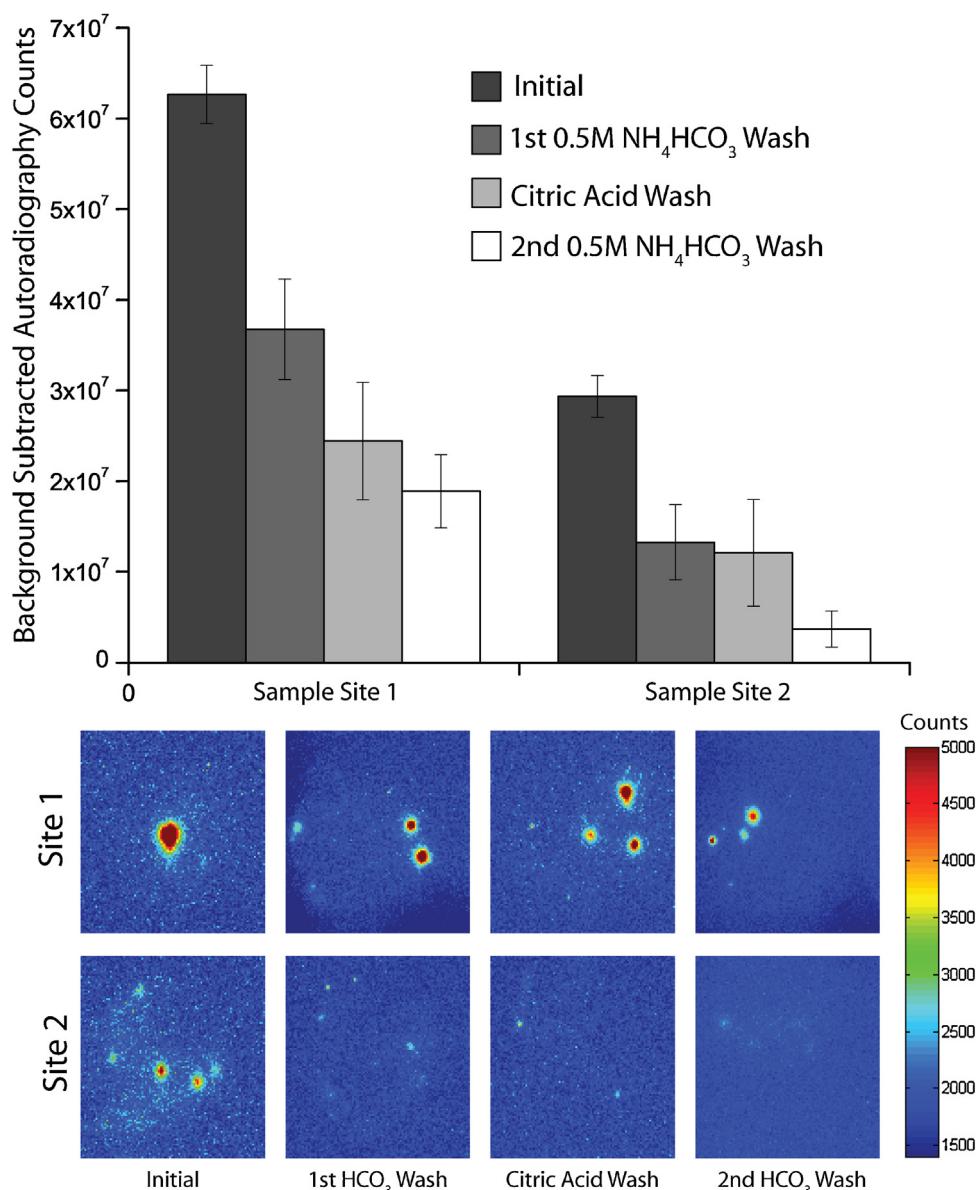


Fig. 6. Net soil radioactivity and representative autoradiographs of soils extracted in a three step sequential batch extraction scheme.

recovery of uranium from these firing range soils can be achieved in batch systems by applying a multi-stage leaching approach.

4. Conclusions

Characterisation of depleted uranium in firing range soils through a combination of microscopic and bulk chemical techniques demonstrates that much of the material persists in primary forms which partition into chemically resistant soil fractions. These findings are consistent with other studies of particles from DU munitions firing, and indicate that this site is a reasonable case study for remediation of DU contaminated soils.

Single step batch extraction demonstrated that low cost, environmentally compatible reagents such as ammonium bicarbonate and citric acid could be applied to effect 40–50% decontamination in small batches of firing range soils, although it remains to be seen if this efficiency carries through to a larger scale. In some cases, this extent of decontamination may be sufficient to allow alternative, less costly management options for contaminated sites, and hence the investigation of larger scales of operation will be of interest.

However, this approach still leaves residual particulate material behind and there is long term uncertainty over the geochemical behaviour and fate of residual DU particles in soil.

Secondary phase formation was observed in NH₄HCO₃ extracted soils, and an extended batch washing procedure was trialled involving alternate washes with bicarbonate and citric acid reagents. This approach successfully removes additional DU from soils, leading to improved (up to 87% removal) efficiency in decontamination. Additional repeat washing in this way begins to approximate an alternating continuous flow system in which the contaminated soil is continually treated with fresh extraction reagent. Such a system may prove more flexible for engineering scale application than alternate batch washing, and future work to improve DU extraction efficiency should investigate continuous flow systems.

Acknowledgements

UK EPSRC is thanked for funding via a studentship for D.E.C. through the Nuclear FiRST DTC (Grant EP/G037140/1). T. Geer (QinetiQ) and C. Toque (DSTL) are thanked for assistance with site

access and soil sampling. P. Lythgoe at the University of Manchester is thanked for assistance with ICP-AES analysis. Part of this work was performed at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland. Access to micro-XAS at Swiss Light Source was funded through the Actinet i3 Integrated Infrastructure Initiative project. NCH is grateful to the Royal Academy of Engineering and Nuclear Decommissioning Authority for funding.

References

- [1] The Royal Society, The Health Hazards of depleted Uranium Munitions – Part 1: Policy Document 6/01, The Royal Society, London, 2002.
- [2] N. Harley, E. Foulkes, L.H. Hilborne, A. Hudson, C.R. Anthony, A Review of the Scientific Literature as It Pertains to Gulf War Illnesses, volume 7: depleted uranium, RAND Corporation, 1999.
- [3] Y.S. Cheng, J.L. Kenoyer, R.A. Guilmette, M.A. Parkhurst, Physicochemical characterization of capstone depleted uranium aerosols II: particle size distributions as a function of time, *Health Physics* 96 (2009) 266–275.
- [4] K.M. Krupka, M.A. Parkhurst, K. Gold, B.W. Arey, E.D. Jenson, R.A. Guilmette, Physicochemical characterization of capstone depleted uranium aerosols III: morphologic and chemical oxide analyses, *Health Physics* 96 (2009) 276–291.
- [5] B. Salbu, K. Janssens, O.C. Lind, K. Proost, P.R. Danesi, Oxidation states of uranium in DU particles from Kosovo, *Journal of Environment Radioactivity* 64 (2003) 167–173.
- [6] B. Salbu, K. Janssens, O.C. Lind, K. Proost, L. Gijssels, P.R. Danesi, Oxidation states of uranium in depleted uranium particles from Kuwait, *Journal of Environment Radioactivity* 78 (2005) 125–135.
- [7] M. Sajih, F.R. Livens, R. Alvarez, M. Morgan, Physicochemical characterisation of depleted uranium (DU) particles at a UK firing test range, *Science of the Total Environment* 408 (2010) 5990–5996.
- [8] O.C. Lind, B. Salbu, L. Skipperud, K. Janssens, J. Jaroszewicz, W. De Nolf, Solid state speciation and potential bioavailability of depleted uranium particles from Kosovo and Kuwait, *Journal of Environment Radioactivity* 100 (2009) 301–307.
- [9] A. Bleise, P.R. Danesi, W. Burkart, Properties, use and health effects of depleted uranium (DU): a general overview, *Journal of Environment Radioactivity* 64 (2003) 93–112.
- [10] S. Handley-Sidhu, M.J. Keith-Roach, J.R. Lloyd, D.J. Vaughan, A review of the environmental corrosion, fate and bioavailability of munitions grade depleted uranium, *Science of the Total Environment* 408 (2010) 5690–5700.
- [11] W.E. Briner, The evolution of depleted uranium as an environmental risk factor: lessons from other metals, *International Journal of Environmental Research and Public Health* 3 (2006) 129–135.
- [12] S. Larson, J. Ballard, V. Medina, M. Thompson, G. O'Connor, C. Griggs, C. Nestler, Separation of Depleted Uranium From Soil, US Army Engineering Research and Development Centre, Environmental Labs, Vicksburg, MS, 2009.
- [13] M. Miller, B. Galloway, G. VanDerpoel, E. Johnson, J. Copland, M. Salazar, An alternative for cost-effective remediation of depleted uranium (DU) at certain environmental restoration sites, *Health Physics* 78 (2000) S9–S12.
- [14] C.P. Farr, T.J. Alecksen, R.S. Heronimus, M.H. Simonds, D.R. Farrar, M.L. Miller, K.R. Baker, Recovery of depleted uranium fragments from soil, *Health Physics* 98 (2010) S6–S11.
- [15] C.C. Choy, G.P. Korfiatis, X.G. Meng, Removal of depleted uranium from contaminated soils, *Journal of Hazardous Materials* 136 (2006) 53–60.
- [16] C.F.V. Mason, W. Turney, B.M. Thomson, N. Lu, P.A. Longmire, C.J. ChisholmBrause, Carbonate leaching of uranium from contaminated soils, *Environmental Science and Technology* 31 (1997) 2707–2711.
- [17] M.C. Duff, C.F.V. Mason, D.B. Hunter, Comparison of acid and base leach for the removal of uranium from contaminated soil and catch-box media, *Canadian Journal of Sport Sciences* 78 (1998) 675–683.
- [18] I.W. Oliver, M.C. Graham, A.B. MacKenzie, R.M. Ellam, J.G. Farmer, Assessing depleted uranium (DU) contamination of soil, plants and earthworms at UK weapons testing sites, *Journal of Environmental Monitoring* 9 (2007) 740–748.
- [19] M. Gavrilescu, L.V. Pavel, I. Cretescu, Characterization and remediation of soils contaminated with uranium, *Journal of Hazardous Materials* 163 (2009) 475–510.
- [20] J.J. Lenhart, S.E. Cabaniss, P. MacCarthy, B.D. Honeyman, Uranium(VI) complexation with citric, humic and fulvic acids, *Radiochimica Acta* 88 (2000) 345–353.
- [21] N. Lu, K.S. Kung, C.F.V. Mason, I.R. Triay, C.R. Cotter, A.J. Pappas, M.E.G. Pappas, Removal of plutonium-239 and americium-241 from rocky flats soil by leaching, *Environmental Science and Technology* 32 (1998) 370–374.
- [22] A.J. Francis, C.J. Dodge, Remediation of soils and wastes contaminated with uranium and toxic metals, *Environmental Science and Technology* 32 (1998) 3993–3998.
- [23] C.W. Francis, M.E. Timpson, J.H. Wilson, Bench- and pilot-scale studies relating to the removal of uranium from uranium-contaminated soils using carbonate and citrate lixivants, *Journal of Hazardous Materials* 66 (1999) 67–87.
- [24] E.J.P. Phillips, E.R. Landa, D.R. Lovley, Remediation of uranium contaminated soils with bicarbonate extraction and microbial U(VI) reduction, *Journal of Industrial Microbiology* 14 (1995) 203–207.
- [25] I.W. Oliver, M.C. Graham, A.B. MacKenzie, R.M. Ellam, J.G. Farmer, Distribution and partitioning of depleted uranium (DU) in soils at weapons test ranges—investigations combining the BCR extraction scheme and isotopic analysis, *Chemosphere* 72 (2008) 932–939.
- [26] A.M. Ure, P. Quevauviller, H. Muntau, B. Griepink, Speciation of heavy-metals in soils and sediments—an account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the commission of the European communities, *International Journal of Environment Analytical Chemistry* 51 (1993) 135–151.
- [27] S.E. Howe, C.M. Davidson, M. McCartney, Determination of uranium concentration and isotopic composition by means of ICP-MS in sequential extracts of sediment from the vicinity of a uranium enrichment plant, *Journal of Analytical Atomic Spectrometry* 17 (2002) 497–501.
- [28] C.C.L. Toque, A.C. Baker, MOD DU Programme—report on the corrosion of depleted uranium in the Solway Firth, UK Defence Science and Technology Laboratory (DSTL), 8th August 2005 CR 11679 V2.0.
- [29] T. Taguchi, C. Broennimann, E.F. Eikenberry, Next generation X-ray detectors for in-house XRD, *Powder Diffraction* 23 (2008) 101–105.
- [30] S.E. Allen, *Chemical Analysis of Ecological Materials*, Wiley, New York, 1974.
- [31] S.R. Brittain, A.G. Cox, A.D. Tomos, E. Paterson, A. Siripinyanond, C.W. McLeod, Chemical speciation studies on DU contaminated soils using flow field flow fractionation linked to inductively coupled plasma mass spectrometry (FLFFF-ICP-MS), *Journal of Environmental Monitoring* 14 (2012) 782–790.
- [32] V. Chazel, P. Gerasimo, V. Dabouis, P. Laroche, F. Paquet, Characterisation and dissolution of depleted uranium aerosols produced during impacts of kinetic energy penetrators against a tank, *Radiation Protection Dosimetry* 105 (2003) 163–166.
- [33] P.R. Danesi, A. Markowicz, E. Chinaea-Cano, W. Burkart, B. Salbu, D. Donohue, F. Ruedenauer, M. Hedberg, S. Vogt, P. Zahradnik, A. Ciurapinski, Depleted uranium particles in selected Kosovo samples, *Journal of Environment Radioactivity* 64 (2003) 143–154.
- [34] S. Handley-Sidhu, P.J. Worsfold, F.R. Livens, D.J. Vaughan, J.R. Lloyd, C. Boothman, M. Sajih, R. Alvarez, M.J. Keith-Roach, Biogeochemical controls on the corrosion of depleted uranium alloy in subsurface soils, *Environmental Science and Technology* 43 (2009) 6177–6182.
- [35] W.H. Johnson, B.J. Buck, H. Brogdon, A.L. Brock, Variations in depleted uranium sorption and solubility with depth in arid soils, *Soil and Sediment Contamination: An International Journal* 13 (2004) 533–544.
- [36] M.C. Duff, J.U. Coughlin, D.B. Hunter, Uranium co-precipitation with iron oxide minerals, *Geochimica et Cosmochimica Acta* 66 (2002) 3533–3547.
- [37] D.J. Wronkiewicz, E.C. Buck, J.K. Bates, Grain boundary corrosion and alteration phase formation during the oxidative dissolution of UO_2 pellets, *MRS Proceedings* 465 (1996).
- [38] R. Vochten, M. Deliens, O. Medenbach, Oswaldpeetersite $(UO_2)_2CO_3(OH)_2 \cdot 4H_2O$, a new basic uranyl carbonate mineral from the Jomac uranium mine, San Juan County, Utah, USA, *Canadian Mineralogist* 39 (2001) 1685–1689.